

Melting and crystallization of in-situ polymerized cyclic butylene terephthalates with and without organoclay: a modulated DSC study

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Abstract. The polymerization of cyclic butylene terephthalate oligomers (CBT) were studied in presence (in 5 wt.%) and absence of an organoclay (Cloisite® 30B) by modulated DSC (MDSC). The organoclay containing samples were produced by dry and melt blending, respectively. The first heating, causing the polymerization of the CBT catalyzed by an organotin compound, was followed by cooling prior to the second heating. The MDSC scans covered the temperature interval between 0 and 260°C. The aim of this protocol was to study the crystallization and melting behavior of the resulting polybutylene terephthalate (pCBT) and its organoclay modified nanocomposites. It was found that the thermal behaviors of the polymerizing and polymerized CBT (pCBT) were strongly affected by the sample preparation. The organoclay suppressed the crystallization of the pCBT produced during the first heating. However, results from the second heating suggest that more perfect crystallites were formed in the organoclay modified pCBT variants. The organoclay also affected the conversion and mean molecular mass of the resulting pCBT which were slightly lower than those of the plain pCBT polymerized under identical conditions.

Keywords: thermal properties, crystallization and melting, cyclic butylene terephthalate (CBT), modulated DSC, organoclay

1. Introduction

Cyclic butylene terephthalate (CBT) oligomers are now available commercially. The related CBT products of Cyclics (Schenectady, N.Y., USA – www.cyclics.com), when molten and catalyzed, polymerize into linear poly(butylene terephthalate) (PBT). The polymerization time can be set in a broad time interval by suitable catalysts ([1] and references therein). Prior to polymerization the melt viscosity of the CBT (melting temperature >140°C) may be as low as 20 mPas [2–3]. This is a

great advantage for liquid composite molding operations where the reinforcement has to be infiltrated, wet-out accordingly (e.g. [4–5]). A further benefit of CBT is that the polymerization can be performed also below the melting temperature of PBT (= 225°C). The industry prefers the isothermal polymerization of CBT at $T = 190^{\circ}\text{C}$. Here the polymerization is followed by the crystallization due to which the solidified product can be removed from the tool without cooling the latter. It is often quoted among further benefits with CBT that its polymerization is athermic (e.g. [1]). In our recent

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work, adopting the technique of modulated differential scanning calorimetry (MDSC), we have concluded that the athermic feature (thermoneutral) is due to the fact that the exothermic polymerization heat is compensated by the endothermic melting of the various CBT oligomers [6]. However, this interpretation may be wrong. Note that when writing the Gibb's law for the polymerization, i.e. $\Delta G = \Delta H - T\Delta S$, the change in the free energy (ΔG) should be negative. The change in the polymerization enthalpy (ΔH) is marginal as both initial oligomers and resulting polymer chains have the same chemical bonds. On the other hand, the linear chains possess a far greater conformational freedom than the constrained CBT cycles initially. So, the large increment in the entropy term (ΔS) is the driving force for the polymerization - which is thus athermic. As a consequence, it is straightforward to use the term 'entropically driven polymerization' for that of the CBT oligomers.

Nowadays, substantial effort are undertaken to produce polymeric nanocomposites using organophilic modified clays. This development is fuelled by drastic property improvements (e.g. stiffness, strength, heat deflection temperature, barrier properties, flame resistance) which can be achieved even at low organoclay content [7]. PBT-based organoclay containing nanocomposites have already been produced by melt blending and in-situ polymerization (e.g. cited works in Ref. [7]). Few reports are even available in the open literature on the polymerization of CBT or similar cyclic polyesters in presence of organoclays [8–9]. Further information about the feasibility of this approach can be taken from the patent literature (e.g. [10]). On the other hand, the thermal behaviors of the polymerizing and polymerized CBT in presence of organoclays have not been studied by the MDSC technique. So, the aim of the present paper was to study the polymerization, crystallization and melting behaviors of CBT and its polymers (denoted further on as pCBT) in presence of a suitable organoclay using the MDSC technique.

2. Experimental

The CBT used was a one-component ready-to-polymerize grade, viz. XB3-CA4 of Cyclics. It contained as catalyst butyltin chloride dihydroxide. As organoclay a methyl-tallow-bis(2-hydroxyethyl) quaternary ammonium salt modified montmoril-

lonite (Cloisite® 30 B), supplied by Southern Clay Inc. (Gonzalez, TX, USA) was selected. The inter-layer spacing of this organoclay was 1.8 nm according to X-ray diffraction results. It is noteworthy that this kind of organoclay was the preferred one in the cited patent [10]. MDSC tests were run on the following CBT and pCBT samples:

- neat CBT (designated as CBT)
- CBT dry blended with 5 wt.% organoclay (designated as CBT + organoclay-dry blend),
- CBT powder melt blended with 5 wt.% organoclay (CBT + organoclay-melt blend), and
- pCBT containing 5 wt.% organoclay after polymerization at $T = 190^\circ\text{C}$ for 30 min (designated as pCBT + organoclay)

It has to be emphasized here that CBT has been polymerized to poly(butylene terephthalate), termed as pCBT in this paper, during the first heating run. The reason behind the above 'sampling' was to explore to what extent the structure-property relationships of the pCBT nanocomposites may be affected by the preparation techniques. Note that premixing of nanoparticles with CBT melt appears as a very promising route as the catalyst in the so-called two-component CBT grades can be added separately in a further step.

The melt blended version was produced by mixing the organoclay in the molten CBT ($T = 160^\circ\text{C}$) for 5 min prior to quenching the compound to room temperature (RT). The resulting materials were powdered in a mortar. Note that the organoclay containing CBT 'dry blend' was 'homogenized' also in the mortar. The organoclay modified pCBT (referred as pCBT + organoclay) was prepared by mixing the organoclay in the CBT melt at $T = 160^\circ\text{C}$ for 5 min before polymerizing in an open poly(tetrafluoro ethylene) mold at $T = 190^\circ\text{C}$ for 30 min. It was established before that the latter conditions produce fully polymerized pCBT. It is noteworthy that both organoclay and CBT were dried prior to use (at $T = 80^\circ\text{C}$ overnight).

MDSC investigations were performed on a TA Instruments-Waters LLC Thermal Advantage for Q-Series equipped with a Q1000 auto-MDSC, connected to a liquid nitrogen cooling system. Scans were recorded from 0 to 260°C . The samples (ca. 6–8 mg) were held at the upper threshold temperature for 5 min. This was followed by cooling and then by a second heating. Both cooling and second heating were performed under the same MDSC conditions as the first heating. The following scan-

ning parameters were set: heating rate of 5°C/min with a modulation of $\pm 0.531^\circ\text{C}/\text{min}$ and a frequency of 40 s under helium flow. The data were analyzed by the Universal Analysis 2000 software package of TA Instruments, Version 4.1D. It has to be emphasized that no efforts were made to study the effects of modulation amplitude, modulation period and heating rate although they may influence the MDSC response markedly.

3. Results and discussion

3.1. CBT (without organoclay)

The MDSC traces registered in the first heating, subsequent cooling and second heating for the (p)CBT are displayed in Figures 1a to c. The order of the deconvoluted MDSC traces from the top to the bottom of all figures is: reversing (R), conventional (C) and non-reversing (NR). Note that the trace C is that one which can be monitored during a conventional DSC measurement. In the NR trace of Figure 1a a broad exothermic peak ($T = 100\dots 150^\circ\text{C}$) is resolved (enthalpy = 21.5 J/g). This peak is likely due to recrystallization phenomena between the various oligomers (dimer, trimer, tetramer etc.) as quoted later. Note that this peak is superimposed to that of the CBT melting based on the related R and C traces (cf. Figure 1a). The next feature of the NR trace is a small endothermic peak at $T = 156^\circ\text{C}$ (enthalpy = 1.4 J/g) that may be linked with the polymerization of CBT to pCBT. In the R and NR traces the onset of crystallization ($T = 200^\circ\text{C}$) followed by melting of the resulting pCBT ($T = 226^\circ\text{C}$) are well resolved. The fact that the crystallization and melting enthalpies are fairly matched is in line with the above assignments. Note that the crystallization is a completely NR process whereas the melting is not – cf. R and NR traces in Figure 1a. The small endothermic peak in the R trace (enthalpy = 1.2 J/g) may be attributed to the presence of some perfect crystals. Figure 1b, displaying the cooling trace, demonstrates that the crystallization is an NR process, in fact. On the R trace in Figure 1b the reverse glass transition (T_g) step is well resolved at $T = 40^\circ\text{C}$. The instability in the R trace (that occurs in all MDSC measurements and marked by a questions mark) is possibly linked with the temperature modulation set. As mentioned earlier the effects of the modulation parameters were not considered in this work. During the sec-

ond heating (cf. Figure 1c) the pCBT formed exhibits a double melting peak. The related exothermic peak (enthalpy = 37.8 J/g) in the NR trace suggests that this double melting is due to massive recrystallization.

3.2. CBT with organoclay (dry blend)

Figure 2 shows the MDSC traces of the CBT + organoclay-dry blend upon first heating, cooling and second heating, respectively. In trace NR of Figure 2a the peak assigned to the recrystallization of the CBT oligomers at $T = 140^\circ\text{C}$ is well detectable. Comparing Figures 2a and 1a two significant effects, caused by the presence of organoclay, can be noticed. First, a double endothermic peak appears in the NR traces ($T = 143$ and $= 155^\circ\text{C}$) which was practically absent for the plain CBT (cf. Figure 1a). This suggests that the recrystallization of the oligomers and/or the polymerization were affected by the organoclay. This note is based on the fact that the organoclay was well intercalated in the corresponding nanocomposites (not presented here). The intercalation affects the conformational possibilities of the molecules, and thus the related entropy change, irrespective whether it happened with the CBT (most probable) or pCBT. Second, the organoclay hinders the crystallization of the pCBT as hardly any crystallization peak can be found in the NR and C traces for the pCBT formed (cf. Figures 2a and 1a). As a consequence, no melting peak appears in the R, C and NR traces. The finding that the organoclay does not act as nucleant for the pCBT crystallization is quite surprising. It was quoted in the literature that this is the primary effect of most organoclays in semi crystalline systems [11]. As pCBT was formed also in this case (cf. Figures 2b and 2c) which, however did not undergo crystallization, one can claim that the polymerization and crystallization of pCBT are consecutive processes. It is noteworthy that the crystallization of pCBT was reported to be kinetically hindered during fast heating scans [12]. The crystallization peak registered during cooling (cf. Figure 2b) is broader than that of the plain pCBT (cf. Figure 1b). In addition, the overall specific enthalpy values are also smaller. During second melting the double melting peak of the pCBT is still present, however, with additional features. In contrast to plain pCBT, the melting peak at higher temperature is more pronounced for the organoclay

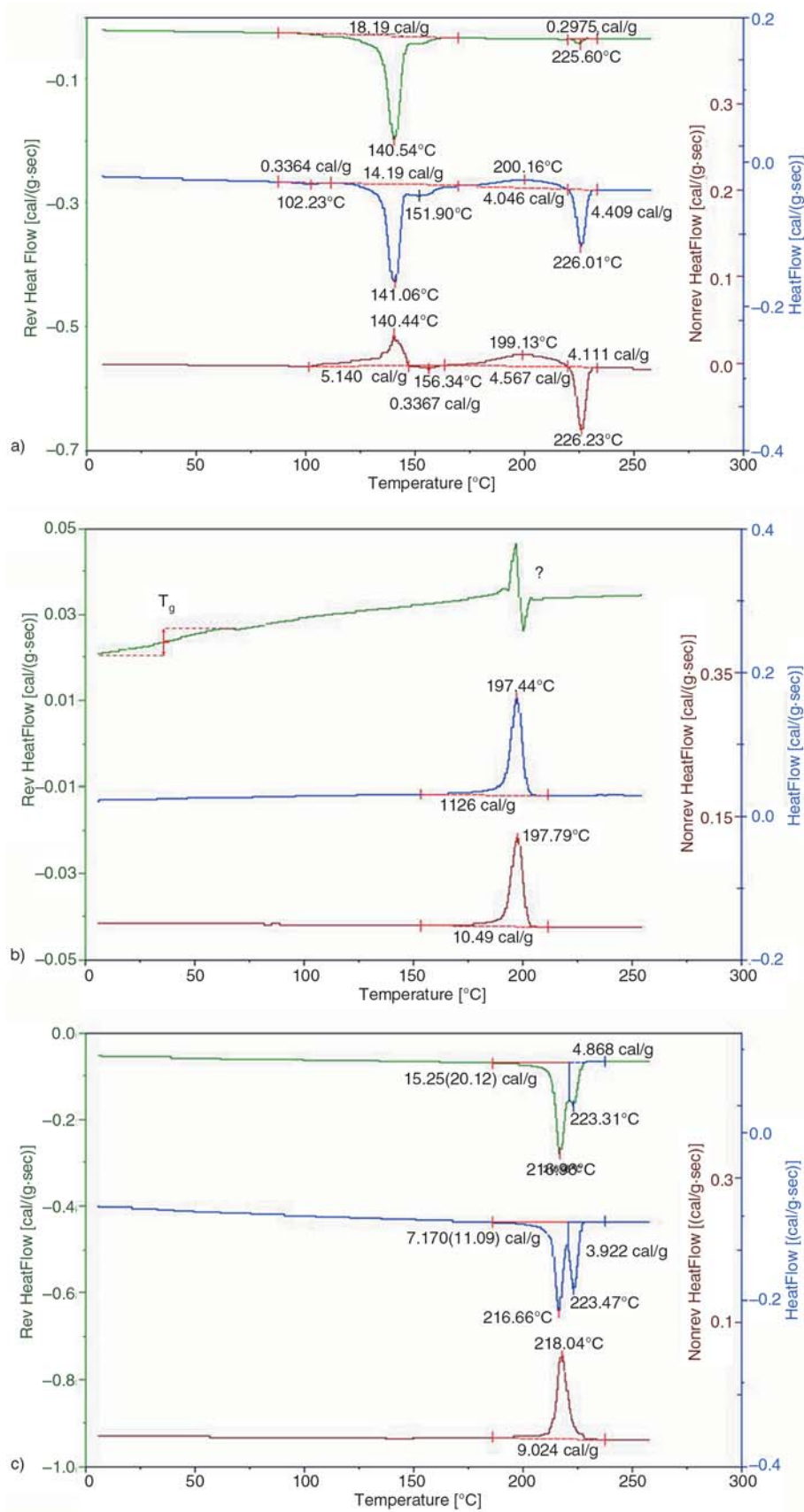


Figure 1. R, C and NR traces monitored during the first heating (a), cooling (b) and second heating (c) for the plain (p)CBT. Notes: The order of the traces is from the top to bottom: R, C and NR, respectively. The related traces show how the peaks were split for the enthalpy determination. To convert cal in J units multiply the former (indicated in the traces) values by 4.184

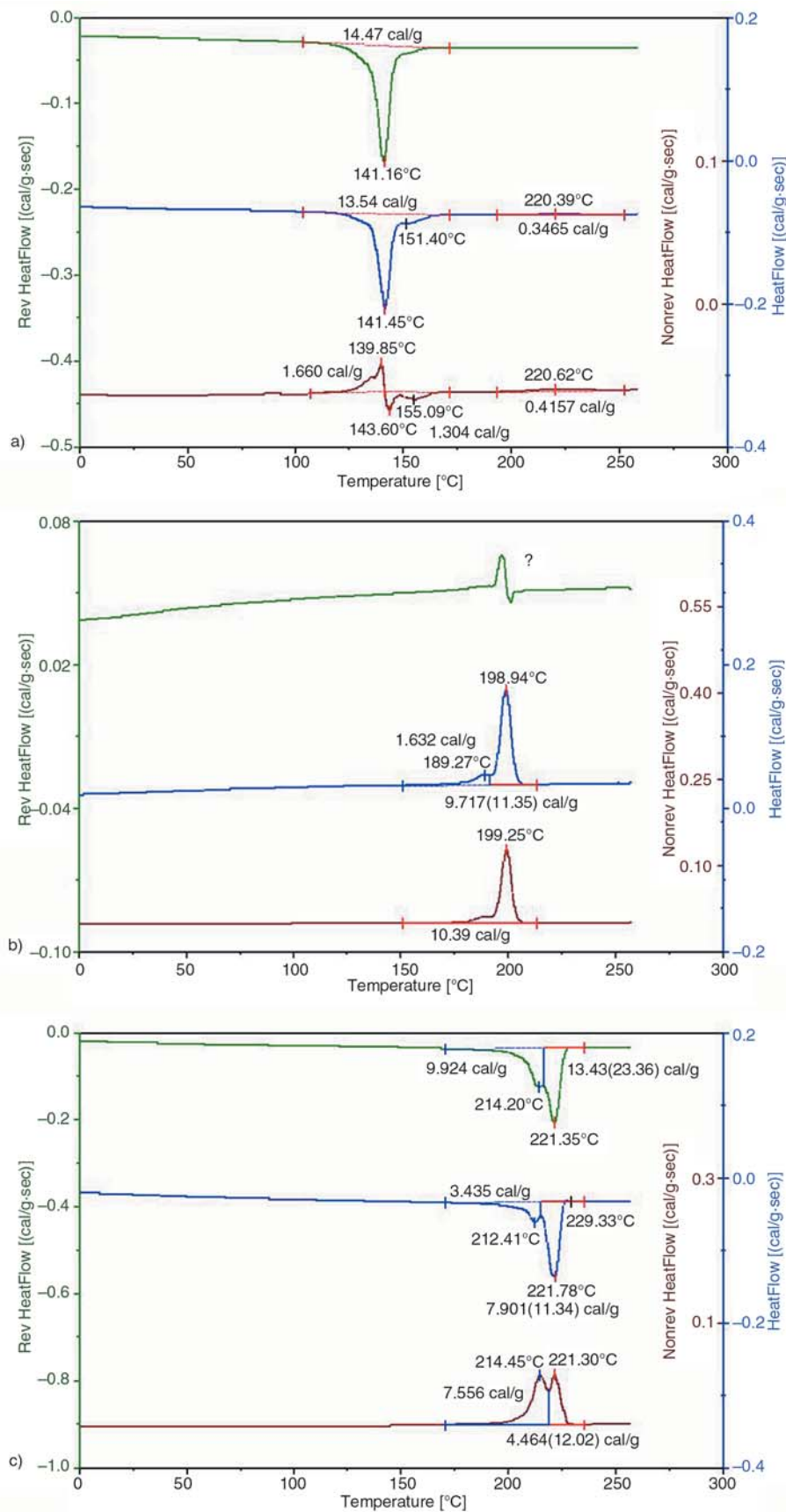


Figure 2. R, C and NR traces monitored during the first heating (a), cooling (b) and second heating (c) for the CBT + organoclay-dry blend. For notes cf. Figure 1

modified version (cf. R and NR traces in Figures 1c and 2c, respectively). This suggests that more perfect crystals were formed which, however, still undergo recrystallization phenomena. The latter is evidenced by the double exothermic peak (which differs again from the plain pCBT) of the NR trace in Figure 2c.

3.3. CBT with organoclay (melt blend)

The first heating scan of the melt blended system shows some further peculiarities (cf. Figure 3a). Both R and C traces display multiple melting peaks, the peak temperature of which is far less than that of the initial CBT ($T = 126$ instead of 140°C , cf. Figure 1a). The melting in this sample starts already at $T = 70^\circ\text{C}$. The corresponding exothermic peak in the NR trace is very broad and shifted to markedly lower temperature when compared to the plain CBT (cf. Figures 3a and 1a). The possible explanations for this finding are listed below. Melt mixing followed by quenching yielded a far less crystalline CBT version. This becomes more and more crystalline due to recrystallization of the corresponding oligomers. Recrystallization phenomena are reflected by the broad exothermic peak ($T = 122^\circ\text{C}$, enthalpy = 32.2 J/g) in the NR trace (cf. Figure 3a). An alternative explanation is that the cyclic oligomers are partly broken up owing to intercalation with the organoclay. This process may be favored by the $-\text{OH}$ groups of the organophilic modifier of the montmorillonite clay used. The resulting compounds may have a lower melting point than the cyclic counterparts. However, it was found that the quenched CBT with yellow/brown color becomes more crystalline and white colored when keeping at sufficient high temperature (but below the melting of the plain CBT). This suggests that the first explanation is the correct one. A similarity with the dry blended version is that the organoclay hampers the crystallization of the pCBT. Note that the crystallization-related exo- and melting-related endothermic peaks in the C and NR traces are practically missing (cf. Figure 3a). This is a similarity with the CBT dry blended with the organoclay (cf. Figure 2a). The peak shapes in the C and NR traces in Figure 3b indicate that the crystallization of pCBT occurs faster and gives more homogeneous crystallites than for the dry blend (cf. Figure 2b). During second heating (cf. Figure 3c) again a double melting peak can be

observed in both R and NR traces. Similar to the dry blend (cf. Figure 2c), one can see again the doubling in the recrystallization peak in the NR trace for this melt blended version (cf. Figure 3c).

3.4. pCBT with organoclay (pCBT + organoclay)

In the DSC traces of this pCBT containing 5 wt.% organoclay (recall that this compound was polymerized at $T = 190^\circ\text{C}$ for 30 min) one can see only the melting of the pCBT (cf. traces R and C in Figure 4a). Albeit the melting peak is very sharp, the melting takes place via recrystallization. This is indicated by the related exothermic peak in the NR trace in Figure 4a. It is interesting to note that before the onset of this exothermic peak in the NR trace, an endothermic peak appears ($T = 222^\circ\text{C}$; enthalpy = 7.3 J/g). This may be linked with some constraint effects that allow the necessary reorganization only after their release. The MDSC traces registered during cooling (Figure 4b) and second heating (Figure 4c) do not offer new insights in the crystallization and melting processes of the pCBT nanocomposites compared to the plain pCBT [6].

It is noteworthy that to check the intercalation/exfoliation of the organoclay was not the scope of this paper. On the other hand, it is essential to give information on whether or not the incorporation of organoclay affected the conversion of the CBT and the mean molecular mass of the corresponding pCBT. So, gel permeation chromatographic (GPC) tests were performed on pCBT and pCBT + organoclay samples polymerized at identical conditions ($T = 190^\circ\text{C}$, time = 30 min). It was found that both conversion (93 instead of 95%) and mean weight average molecular mass data (91.3 instead of 104 kDa) were reduced slightly by incorporation of the organoclay. It is worth of noting that the organophilic modifier of the clay may strongly influence both conversion and molecular mass characteristics. Using an organophilic montmorillonite with primary amine (viz. octadecylamine) intercalant a conversion of only ca. 70% was reached.

4. Conclusions

Based on this work devoted to study the MDSC response of polymerizing and polymerized cyclic butylene terephthalate (CBT and pCBT, respec-

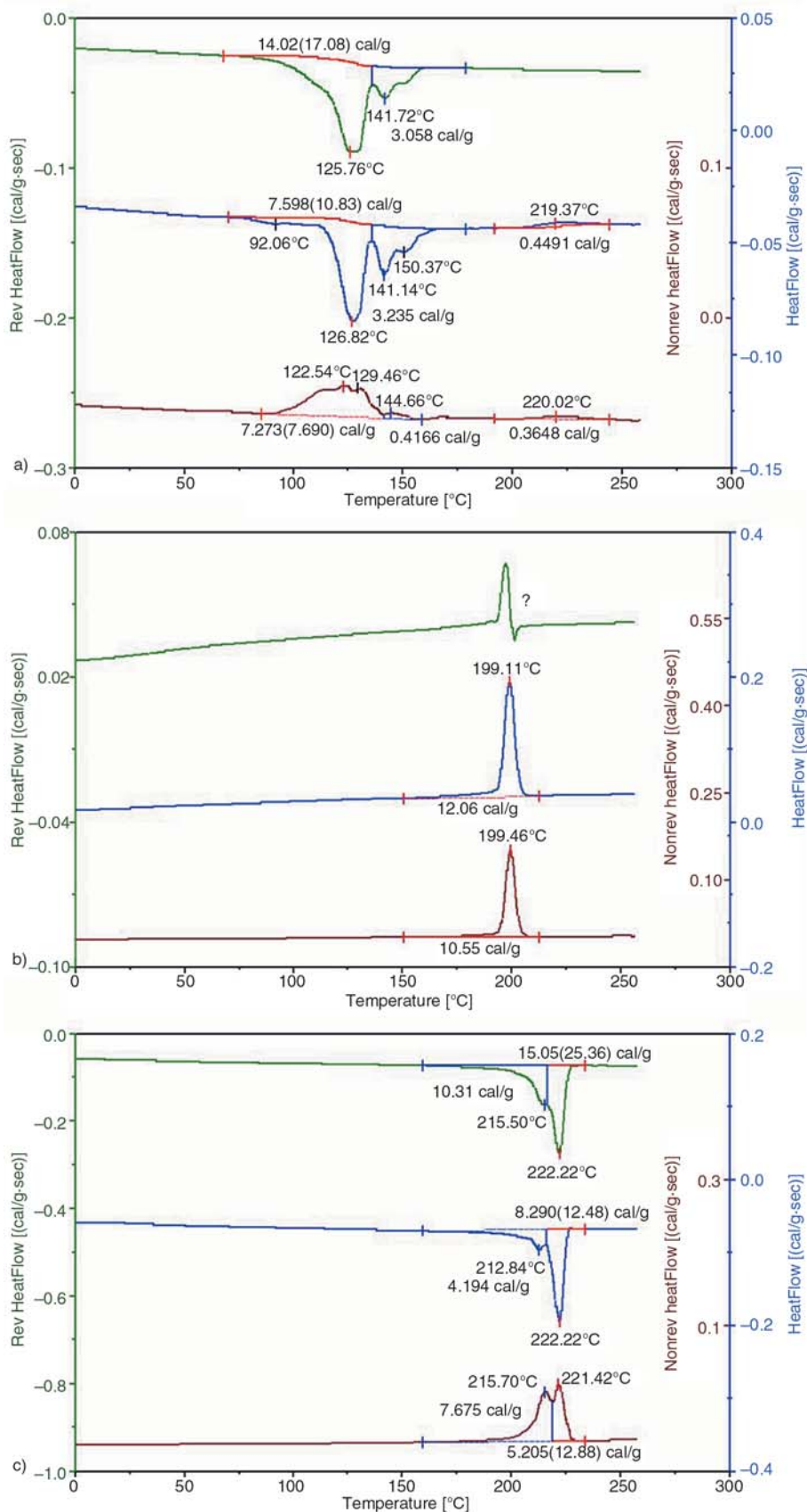


Figure 3. R, C and NR traces monitored during the first heating (a), cooling (b) and second heating (c) for the CBT + organoclay-melt blend. For notes cf. Figure 1

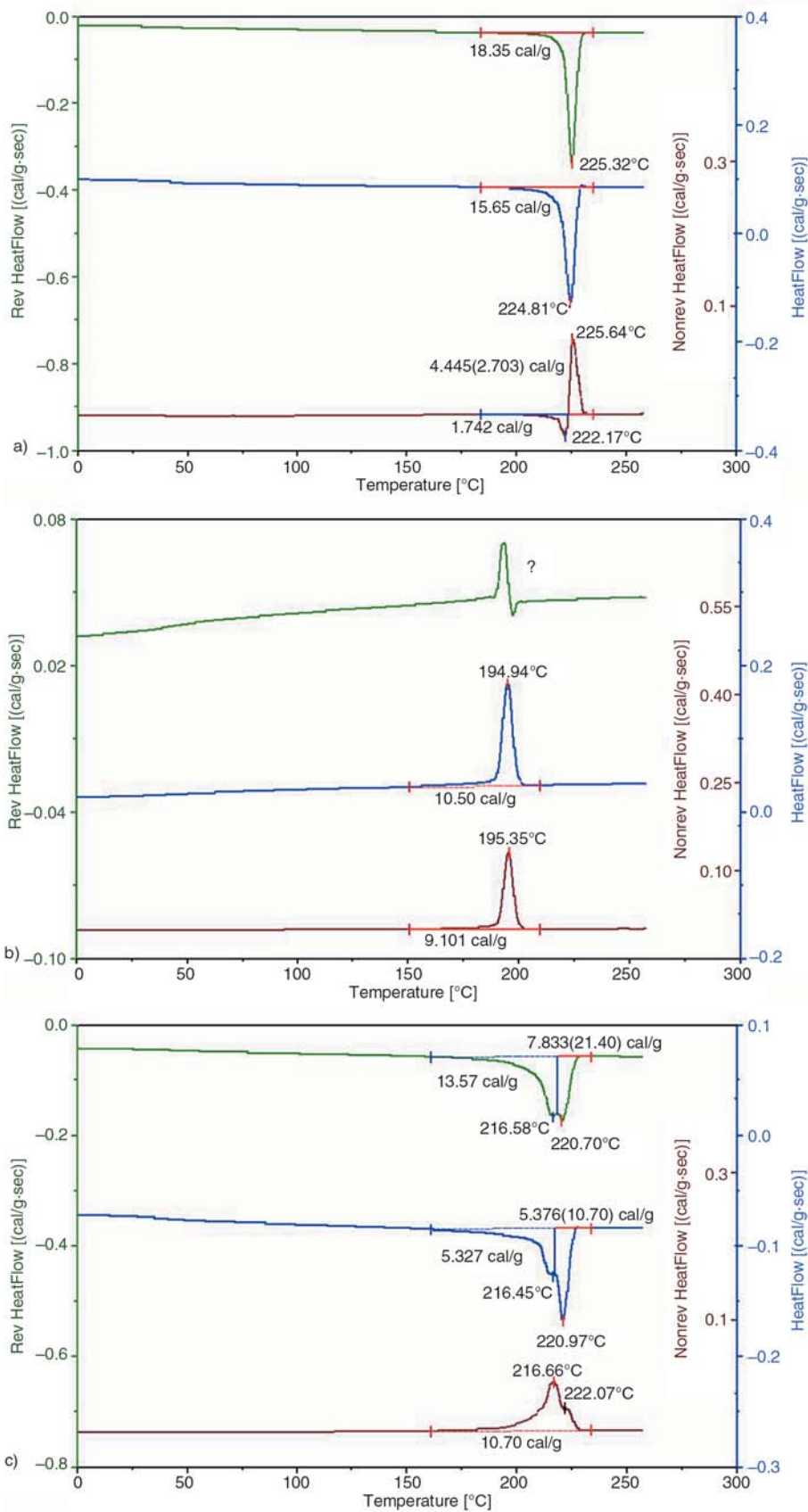


Figure 4. R, C and NR traces monitored during the first heating (a), cooling (b) and second heating (c) for the pCBT + organocaly. For notes cf. Figure 1

tively) in absence and presence of an organoclay (Cloisite® 30B incorporated in 5 wt.%), the following conclusions can be drawn:

- the preparation of the samples influences the crystallization and melting behaviors of the in-situ polymerized pCBT systems. On the other hand, the molecular mass characteristics and conversion are less affected by the organoclay used.
- the organoclay reduces the crystallization ability of the pCBT but likely produce more perfect crystals. As the crystalline structure of pCBT is very complex (e.g. [13]), this aspect has to be checked by X-ray diffractions measurements.
- melt blending with organoclay followed by quenching strongly alter the crystalline morphology of the CBT oligomers that should be clarified also through X-ray diffraction. Nevertheless, melt mixing of nanoparticles (any kind) with uncatalyzed CBT prior to introducing the catalysts may be an interesting route to produce nanocomposites.

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References

- [1] Brunelle D. J.: Synthesis and polymerization of cyclic polyester oligomers. in 'Modern Polyesters' (eds.: Scheirs J. and Long T. E.), Wiley, Chichester, 117–142 (2003).
- [2] Tripathy A. R., MacKnight W. J., Kukureka S. N.: In-situ copolymerization of cyclic poly(butylene terephthalate) oligomers and ϵ -caprolactone. *Macromolecules*, **37**, 6793–6800 (2004).
- [3] Mohd Ishak Z. A., Gatos K. G., Karger-Kocsis J.: On the in-situ polymerization of cyclic butylene terephthalate oligomers: DSC and rheological studies. *Polymer Engineering and Science*, **46**, 743–750 (2006).
- [4] Parton H., Verpoest I.: In-situ polymerization of thermoplastic composites based on cyclic oligomers. *Polymer Composites*, **26**, 60–65 (2005).
- [5] Mohd Ishak Z. A., Leong Y. W., Steeg M., Karger-Kocsis J.: Woven glass fabric composites via in-situ polymerized cyclic butylene terephthalate oligomers. *SPE-ANTEC*, 186–189 (2006).
- [6] Mohd Ishak Z. A., Shang P. P., Karger-Kocsis J.: A modulated DSC study on the in-situ polymerization of cyclic butylene terephthalate oligomers. *Journal of Thermal Analysis and Calorimetry*, **84**, 637–641 (2006).
- [7] Utracki L. A.: Clay-Containing Polymer Nanocomposites, Vols. 1–2, Rapra Technology, Shawbury (2004).
- [8] Tripathy A. R., Burgaz E., Kukureka S. N., MacKnight W. J.: Poly(butylene terephthalate) nanocomposites prepared by in-situ polymerization. *Macromolecules*, **36**, 8593–8595 (2003).
- [9] Lee S.-S., Ma Y. T., Rhee H.-W., Kim J.: Exfoliation of layered silicate facilitated by ring-opening reaction of cyclic oligomers in PET-clay nanocomposites. *Polymer*, **46**, 2201–2210 (2005).
- [10] Barger M., Walia P., Dion R. P., Paquette M. S., Bank D. H., Lebaron P. C., Read M. D., Oelberg J. D.: Polymerized macrocyclic oligomer nanocomposite compositions. WO 2004/058868, USA (2003).
- [11] Karger-Kocsis J., Zhang Z.: Structure-property relationships in nanoparticle/semicrystalline thermoplastic composites. in 'Mechanical Properties of Polymers Based on Nanostructure and Morphology' (eds.: Michler G. H. and Baltá Calleja F. J.), CRC Press, Boca Raton, 553–602 (2005).
- [12] Mohd Ishak Z. A., Leong Y. W., Steeg M., Karger-Kocsis J.: Mechanical properties of woven glass fabric reinforced in situ polymerized poly(butylene terephthalate) composites. *Composites Science and Technology*, **67**, 390–398 (2007).
- [13] Parton H., Baets J., Lipnik P., Goderis B., Devaux J., Verpoest I.: Properties of poly(butylene terephthalate) polymerized from cyclic oligomers and its composites. *Polymer*, **46**, 9871–9880 (2005).